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Applied Polarography for Analysis of Ordnance Materials.

Part 3. Field Tests of NWC Digital Polarograph and Pollution Monitoring System

by
Gerald C. Whitnack
Research Department

JANUARY 1979

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FOREWORD

The work presented in this report is part of a continuing research project entitled "Applied Polarography for Analysis of Ordnance Materials." This work is supported by the Naval Sea Systems Command, Code 0332, under Task Area No. SF57572301 and represents a final report on Phase II of the work which covers field tests conducted during May and June of fiscal year 1977.

The field tests were made with the Solid-State Field Polarograph developed at the Naval Weapons Center for monitoring organic pollutants in effluent water. The tests were held at the Naval Torpedo Station, Keyport, Washington, and at the Naval Magazine Area, Lualualei, Hawaii, respectively, in connection with the waste disposal and pollution abatement responsibilities for the Mk 48 torpedo.

Phase I of this work is divided into two final reports under the above general title. Part 1 is "Determination and Monitoring of 1,2-propyleneglycoldinitrate in Effluent Water by Single-Sweep Polarography," and Part 2 is "An Inexpensive Solid-State Field Polarograph With Digital and Analog Output."

This report has been reviewed for technical accuracy by Dr. Arnold T. Nielsen.

Approved by
E. B. ROYCE, *Head*
Research Department
10 January 1979

Under authority of
W. L. HARRIS
RAdm., U. S. Navy
Commander

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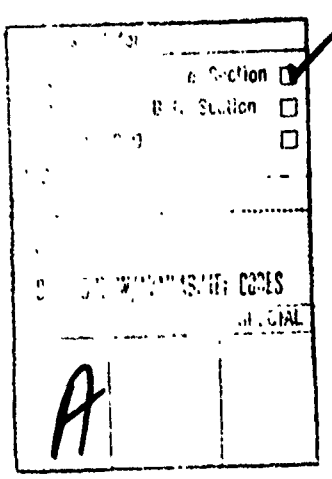
(U) *Applied Polarography for Analysis of Ordnance Materials. Part 3. Field Tests of NWC Digital Polarograph and Pollution Monitoring System*, by Gerald C. Whitnack. China Lake, Calif., Naval Weapons Center, January 1979. 16 pp. (NWC TP 5860, Part 3, publication UNCLASSIFIED.)

(U) A portable polarograph and pollution monitoring system, developed at the Naval Weapons Center (NWC) and described in Parts 1 and 2 of NWC TP 5860, was subjected to a series of field tests. These tests were conducted during May and June 1977 in connection with the waste disposal and pollution abatement responsibilities for the Mk 48 torpedo. The tests were made at the Naval Torpedo Station (NTS), Keyport, Washington, and at the Naval Magazine Area in Lualualei, Hawaii.

(U) The polarographic system monitored the nitrate esters 1,2-propyleneglycoldinitrate (PGDN) and/or propyleneglycolmononitrate (PGMN) in effluent water produced by a Wastewater Reclamation and Purification System designed by the Navy to efficiently remove the pollutants from *Otto Fuel* wastewater. 1,2-Propyleneglycoldinitrate and/or PGMN levels of <0.1 to 0.5 mg/liter were successfully determined in the effluent water by the polarograph directly on-site.

(U) This report describes and discusses the above field tests, presents polarographic data obtained in the field, and suggests the use of such equipment in the determination and monitoring of ordnance-derived pollutants. Recommendations are given for future work with polarographic field monitoring systems. These systems have been shown in this work as unique in their ability to rapidly analyze, *on-site*, for both PGDN and PGMN in the same aliquot of an effluent water. At present, there is no other instrumentation that can be used in the field for an *on-site* analysis of both nitrate esters.

(U) This study suggests that PGMN is a major pollutant and should be monitored along with PGDN in effluent water produced by Wastewater Purification Systems designed to remove PGDN from *Otto Fuel* wastewater.



CONTENTS

ACKNOWLEDGMENT

The author greatly appreciates the assistance of personnel from the Naval Underwater Systems Center, the Naval Torpedo Station, the Naval Surface Weapons Center, and the Naval Civil Engineering Laboratory in operation of the purification system, in furnishing samples of effluent and sump water, arranging for the on-site tests, and finally, for chromatographic analysis of water samples and preparation of some pure nitrate esters for analytical studies.

Special thanks are expressed to Walter J. Becktel of this Center for technical assistance in the design and construction of the field polarograph, to Arnold T. Nielsen of this Department for preparation of propyleneglycolmononitrate, to Reggie Narciso of the Naval Underwater Systems Center, and Richard Saam of the Civil Engineering Laboratory for continued interest and support of the tests, and finally, to the Naval Sea Systems Command, Code 033, for initial interest and financial support of this work.

INTRODUCTION

The portable polarograph and pollution monitoring system developed at the Naval Weapons Center (NWC), for the determination and monitoring of contaminants in effluent wastewater (from explosive processing plants and ordnance demilitarization facilities),[1] was recently subjected to *field tests* at two Navy sites. These sites were the Naval Torpedo Station (NTS), Keyport, Washington, and the Naval Magazine site at Lualualei, Hawaii, respectively. These tests were made in connection with the waste disposal and pollution abatement responsibilities for the Mk 48 torpedo. The tests at NTS were conducted in May 1977, while the tests at Lualualei were made from 15 through 24 June 1977.

The polarographic equipment tested was designed for field use to determine and monitor the nitrate esters 1,2-propyleneglycoldinitrate (PGDN) and/or propyleneglycolmononitrate (PGMN) in effluent water produced from a Wastewater Reclamation and Purification System designed and developed by the Navy. The purification system used in this work was an activated carbon adsorption process designed to remove PGDN from *Otto Fuel* wastewater to concentration levels of 1.0 mg/liter. A Naval Underwater Systems Center (NUSC) report[2] illustrates and describes the purification system and summarizes the results of the *field tests* made at Lualualei. At Keyport, a purification system similar to the NUSC system was tested. This system was a modified NUSC design built by the Civil Engineering Laboratory (CEL), Port Hueneme, California, and was operated by personnel from CEL and NTS.

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[1] Naval Weapons Center. *Applied Polarography for Analysis of Ordnance Materials, Part 1,* by G. C. Whitnack and W. J. Becktel. China Lake, Calif., NWC, June 1976. 20 pp. (NWC TP 5860, Part 1, publication UNCLASSIFIED.); Naval Weapons Center. *Applied Polarography for Analysis of Ordnance Materials, Part 2,* by W. J. Becktel and G. C. Whitnack. China Lake, Calif., NWC, September 1976. 18 pp. (NWC TP 5860, Part 2, publication UNCLASSIFIED.)

[2] Naval Underwater Systems Center. *Development of the NUSC Waste Water Reclamation and Purification System,* by R. T. Narciso. Newport, Rhode Island, NUSC, September 1977. (NUSC TM 77-2151, publication UNCLASSIFIED.)

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A vapor-phase chromatography method of analysis for PGDN, developed by John Hoffsommer[3] of the Naval Surface Weapons Center (NSWC), White Oak, Maryland, was used at Keyport by NTS personnel for the analysis of the effluent water produced by the purification system. The analysis was made in the NTS laboratory on *grab samples* of the effluent water. At Lualualei no laboratory was available. Thus, an on-site chromatographic analysis of the effluent for PGDN was not possible. The NWC field polarograph provided the only analytical data for PGDN and PGMN at this site.

This report describes *in brief* the operation of a satisfactory carbon adsorption system for the removal of PGDN from *Otto Fuel* wastewater. A rapid and accurate polarographic analysis, with a digital polarograph and monitoring system for field use, is presented for the direct analysis of PGDN and/or PGMN in the effluent water produced in the carbon adsorption system. Satisfactory analytical data obtained with the polarographic monitoring system at field sites are presented. The *field test* results are discussed and recommendations are given for future action toward the development and use of this simple, rapid, and versatile field monitoring system for pollution abatement studies of ordnance-derived materials.

EXPERIMENTAL

WASTEWATER RECLAMATION AND PURIFICATION SYSTEM

The effluent water monitored by the polarograph was obtained from the carbon adsorption system referred to in the introduction of this report. The purification system had to furnish effluent water that complied with the NUSC criterion currently set at 1 mg/liter (ppm) of *Otto Fuel*. The *Otto Fuel* is monitored as PGDN by the polarograph. 1,2-Propyleneglycoldinitrate is the main ingredient in *Otto Fuel* (95-98%). The carbon system consisted of two separate sections: an Oily Water Separator Assembly and a Carbon Column Assembly. The Oily Water Separator Assembly consisted of a variable speed motor and pump combination, an oily water separator cylinder, a prefilter, an emulsion breaker, and manual discharge valves. The Carbon Column Assembly consisted of four plexiglas columns approximately 210 centimeters (seven feet) by 20 centimeters (eight inches) in diameter. The assembly was mounted on a steel frame.

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[3] J. C. Hoffsommer. "Quantitative Analysis of Nitro Compounds in the Micro- to Picogram Range by a Combination of Thin-Layer and Vapor Phase Chromatography With the Nickel-63 Electron Capture Detector," *J. Chromatogr.*, Vol. 51 (1970), pp. 243-51.

The system drew waste liquid (sump water) containing *Otto Fuel* from an underground sump at the site of operation and processed waste liquid to a rate of 9.5 liters (2.5 gallons) per minute. The polarographic measurement can be made directly at various points in the cleanup system and/or in the final effluent water as it flows from the system during operation. The analysis can be made periodically from a *grab sample* or in a continuous manner with the digital polarograph and flow-through polarographic cell.

The carbon used in the process was Filtrasorb-400 activated carbon. Each column was filled with the carbon over a bed of commercial grade *Pea Gravel*. The effective life of the carbon in this process appeared to be a period of 9 hours of continuous operation, during which approximately 5,130 liters (1,350 gallons) of *Otto Fuel* wastewater were passed through the carbon. The carbon column system was then cleaned and the columns again filled with fresh carbon for the next cleanup operation.

POLAROGRAPHIC ANALYSIS

A. Sample Effluent or Sump Wastewater Analysis

A 2 ml aliquot of sampled effluent or diluted sump wastewater (1 ml to 100 ml with 0.1 M NaCl) was placed in a 5 ml polarographic cell, to which had been added a small volume of chemically pure mercury to serve as an anode; a dropping mercury electrode (DME) was inserted into the cell solution and oxygen-free nitrogen or Freon gas was bubbled slowly through the cell solution for 3-5 minutes to remove dissolved oxygen. The start potential of the polarograph was set between -0.05 and -0.20 volt (depends upon PGDN wave definity) and the polarogram was recorded. The peak potential for the first wave of PGDN was seen between -0.45 and -0.60 volt. This wave represented the reduction of PGDN at a DME to PGMN. The start potential of the polarograph was then reset to between -0.40 and -0.60 volt (depends upon PGDN wave definity) and a polarogram was recorded. The peak potential for the second wave of PGDN was seen between -0.80 and -0.95 volt. The second wave represented the reduction of PGMN formed during the reduction of PGDN in the first wave plus any additional PGMN that might be present in the effluent. If the two waves are equivalent in height then only PGDN is present in the sample. When PGMN alone is present in a sample, only the second wave is observed. The amount of PGDN in a sample may be calculated from either wave if no PGMN is present. The height of the second wave can be used to calculate the total amount of PGDN and/or PGMN that is present in an effluent sample. Standard solutions of pure PGDN and PGMN, respectively, were prepared in the 10^{-5} g/ml range and micro-aliquots of these (0.01 to 0.05 ml) were added to the polarographic cell solution for calculations by *standard addition*[4] of the amount of PGDN and/or PGMN present. This

[4] G. C. Whitnack. "Single-Sweep Polarographic Techniques Useful in Micropollution Studies of Ground and Surface Waters," *Anal. Chem.*, Vol. 47 (1975), pp. 618-21.

was done from a ratio of the wave heights of the sample solution alone and the sample solution with added PGDN and/or PGMN. A linear calibration curve of wave height vs. PGDN concentration can be used with most final effluents (water from last carbon column); however, if the effluent water is taken at various points in the system during the cleanup operation, the method of *standard addition* is preferred because of the possible effect of a changing matrix on the wave heights. The addition of a finite amount (0.1 to 0.5 molar) of NaCl to each effluent sample analyzed usually allows the use of a calibration curve for the calculation of PGDN and/or PGMN in this work.

B. Periodic or Continuous Flow-Through Cell Analysis

The polarographic cell designed for periodic or continuous flow-through analysis[1,5] was used for this type of field analysis of the nitrate esters (PGDN and PGMN). The general analytical procedure given in part A of the Experimental Section was followed. The cell was placed on-line at a cleanup site, with convenient plumbing, to allow a periodic or continuous flow of the carbon column effluent water into and out of the cell. The cell was placed inside a small metal cylinder that maintained a constant temperature (± 0.2°C) of the sample solution.[1,5] When used with a DME, the amount of mercury used with this cell is about 10 ml of mercury in 40 hours of operation and the volume of effluent in the cell is about 10-15 millliliters per analysis. Very little data to date have been obtained in the field with this type of cell. However, in the NWC laboratory, trial experiments with solutions of known concentrations (ppb) of PGDN added to a typical effluent water (that by polarographic analysis showed no PGDN to be present) were shown to give linear results with a DME in the flow-through cell. Both static and slow-flow conditions were investigated in the laboratory and gave satisfactory data.

C. Solid Electrode Analysis

Current research in this laboratory is showing a great deal of promise for the use of solid-type electrodes (glassy carbon, pyrolytic graphite, etc.) as replacement electrodes for the DME with the digital polarograph and monitoring system described in this report. The development of such electrodes can increase the use of polarographic methods of analysis in the field, where the use of a DME sometimes restricts the method because of the need of scientifically trained personnel in field operation of the equipment. Mercury is also a toxic substance and a DME is cumbersome to use in the field. A solid-type electrode is ideally suited for continuous on-site single-sweep polarographic analysis of organic pollutants in a flowing stream of effluent water. Under the

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[5] G. C. Whitnack in *Identification and Analysis of Organic Pollutants in Water*, Chapter 18, L. H. Keith, ed. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1976, pp. 265-79.

single-sweep and flow conditions used in this analytical procedure, the reduction products at the solid electrode surface are rapidly and efficiently removed prior to each voltage sweep; thus, the surface of the electrode is renewed for each voltage sweep (similar to that produced by a DME) and excellent reproducibility of the current-voltage curve occurs.

RESULTS AND DISCUSSION

The analytical data presented in this report were obtained during *field tests* of the Wastewater Reclamation and Purification System described herein. Most of the polarographic data were obtained on-site with the digital polarograph and monitoring system. Some *grab sample* data are reported on water samples that were analyzed with a research polarograph at NWC. The chromatographic data were obtained with a research chromatograph in the laboratory at Keyport by NTS personnel. These analyses were made on *grab samples* obtained at the Keyport cleanup site. At Lualualei, only polarographic data obtained with the NWC digital polarograph on-site were available to evaluate the efficiency of the purification system.

Table 1 shows the polarographic data obtained on the effluent water at the Lualualei site on two runs with the NUSC purification system.

TABLE 1. Polarographic Analysis of PGDN in *Otto Fuel* Wastewater Effluent (From Carbon Cleanup System).

Effluent sample[a]	Digital polarograph (at site, mg/liter)	Research polarograph (in NWC lab, mg/liter)
First run		
No. 1 (75 gal)	0.11	0.15
No. 2 (300 gal)	0.26	0.23
No. 3 (525 gal)	0.12	0.15
Second run		
No. 1 (150 gal)	0.23	0.21
No. 2 (525 gal)	0.14	0.20
No. 3 (825 gal)	0.29	0.32
No. 4 (1125 gal)	0.40	0.42

[a] Final effluent from system.

The data in column 1 were obtained on-site with the digital polarograph, while that in column 2 were obtained on aliquots of the same samples with a research polarograph at NWC.[4] The results check very well considering the samples analyzed at NWC were bottled at the site and brought back to NWC for analysis. From the data obtained in these studies it appears that at least 1,100 gallons of *Otto Fuel* wastewater (sump water) can be run through the NUSC purification system without exceeding the limit of 1.0 mg/liter (ppm) finally established by NUSC for the PGDN concentration in the effluent water that flows from the NUSC system to the environment. However, the total number of gallons of *Otto Fuel* wastewater that can safely be run through a particular carbon adsorption system will likely vary and greatly depend upon the amount of foreign material and PGDN and PGMN in the wastewater. Thus, an on-line monitoring device, like the polarograph described in this work, is essential to each purification system to ensure that at all times an established safe concentration level for PGDN and/or PGMN is not exceeded in the final effuent from the system.

Data shown in Table 2 were obtained at Keyport with the digital polarograph and show the variation in PGDN concentration in the effluent water at various points in the carbon cleanup system during a field run of the CELNTS purification system. The final effluent appears to be within the 1.0 ppm limit established for PGDN, although the PGDN concentration in the water flowing from each carbon column in the system varied considerably.

TABLE 2. Field Polarographic Analysis for PGDN in Water Produced in Carbon Column Adsorption Studies (Samples Taken at Different Points in *Otto Fuel* Purification System).

Sample no.		PGDN, mg/liter
Effluent, final	8390	0.12
Effluent, final	7890	0.37
Col. no. 2	7890	0.37
Col. no. 2	8390	2.06
Col. no. 1A (meter)	4910	1.91
Col. no. 1A (880 gal)	4850	1.54
Col. no. 1	7790[a]	167.--
Feed	7810[a]	1,062.--

[a] Sample diluted 1 ml to 100 ml water for analysis.

A comparison of data for the analysis of PGDN in effluent water by the polarographic and chromatographic methods of analysis, respectively, is given in Table 3. The chromatographic data show that all samples contain very low amounts of PGDN. The polarographic data show three samples to have more than 0.10 ppm of PGDN. It is believed that the polarographic data are higher for these samples because the polarograph analyzes for the amount of both PGMN and PGDN that are present. The data shown in the table thus represent the total concentration of PGMN plus PGDN in these samples. The chromatograph cannot analyze for PGMN with the NSWC analytical procedure used in this work and the chromatography data in the table represent only the PGDN content of the sample. Propyleneglycolmononitrate is probably as toxic as PGDN and should be included in any analytical method used to determine and monitor these toxic substances in effluent and natural water. 1,2-Propyleneglycoldinitrate can hydrolyze readily in sump water during storage and also during the cleanup operation of the purification system to form PGMN. Some of the samples analyzed by polarography in this work showed values as high as 0.5 ppm of PGMN.

TABLE 3. Analysis of PGDN and PGMN in Effluent Water[a] (Polarography[b] and Chromatography[c]).

Sample no.	Polarography, mg/liter	Chromatography, mg/liter
1D-A	<0.05	0.003
2D-A	<0.05	0.002
4D-A	<0.05	0.001
1D-B	<0.05	0.002
2D-B	0.12	0.005
1D-C	0.23	0.085
4D-C	0.26	0.102

[a] Final effluent from carbon cleanup system of *Otto Fuel* wastewater.

[b] Single-sweep at NWC (PGDN and PGMN).

[c] Vapor-phase at NTS (PGDN only).

Typical single-sweep polarograms in effluent water obtained with the digital polarograph and analytical procedure described in this report are shown in Figure 1. The six curves represent two repetitive sets of data (three each) from two separate aliquots of the same sample of effluent water to which was added 0.20 ppm PGDN. The PGDN was added to an effluent sample which contained no polarographic measurable PGDN. Note the excellent reproducibility of both the analog (X-Y recorder) data and the digital counts produced by the field polarograph and monitoring system. A comparison of the analog data and the digital data for a slight change in PGDN concentration is shown in Table 4. A change in digital count of 10[0] represents a change in PGDN concentration of 0.02 mg/liter (0.02 ppm), thus increasing the sensitivity of the method.

TABLE 4. Digital and Analog Data Comparison (Digital Polarograph, pH 7.30 Sample of Effluent).

PGDN added, mg/liter	X-Y recorder,[a] graph paper divisions	Digital count,[b] cell current 11
0.19	8.0	1.205
0.21	9.0	1.312
0.24	10.0	1.407
0.29	12.0	1.628

[a] Moseley 2-D.

[b] Digital polarograph, average of six counts.

The polarographic reduction of R-O-NO_2 has been shown previously to produce RO^- plus NO_2^- and, finally, R-OH.[6] The overall reduction mechanism of PGDN and PGMN at a DME in effluent water of the type studied in this research is shown in Figure 2. The effluent water studied in this work had a pH range of 6 to 8 and in this water PGDN reduces at the DME in two steps. The first step is a two-electron change to PGMN followed by the second step of two electrons (of the formed PGMN) to propyleneglycol (PG). If only PGMN is present in the effluent water, a single wave (two electrons) is observed at the same voltage as the second wave seen with PGDN. The 1- and 2-isomers of PGMN have peak potentials very close, as no separation of waves was observed with the sample of PGMN used in this work. The PGMN was shown to be a mixture of the isomers by nuclear magnetic resonance (NMR) assay.

Figure 3 shows a sample of Lualualei sump water that was diluted with tap water from Lualualei for polarographic analysis with the digital instrument. Two waves are seen with this sample, but the second wave height (curve 2) is considerably larger (2-1/2 times) than the first wave height (curve 1). Thus it can be seen that there is some PGMN originally present in this sample.

Figure 4 shows a series of curves representing the standard addition of PGDN to a diluted sump sample taken at Lualualei. These polarograms are drawn on 10 x 10 to 1/2-inch graph paper with a Moseley 2D X-Y recorder directly from the digital polarograph. They represent *standard additions* from 1 to 5 ppm of PGDN. Note the good linear relationship of the well-defined polarograms in this concentration range. At this sensitivity setting of the instrument (cell current = 7), a zero baseline current, through the voltage region scanned by the polarograph, is obtained. The digital number shown in the easy view window of the polarograph is reproducible to within 1 to 2% for a given concentration, and shows a good linear relationship for number vs. concentration of PGDN.

[6] F. Kaufman, H. J. Cook and S. M. Davis. "The Electrolytic Reduction of Simple Nitrate Esters, *J. Am. Chem. Soc.*, Vol. 74 (1952), pp. 4997-5001.

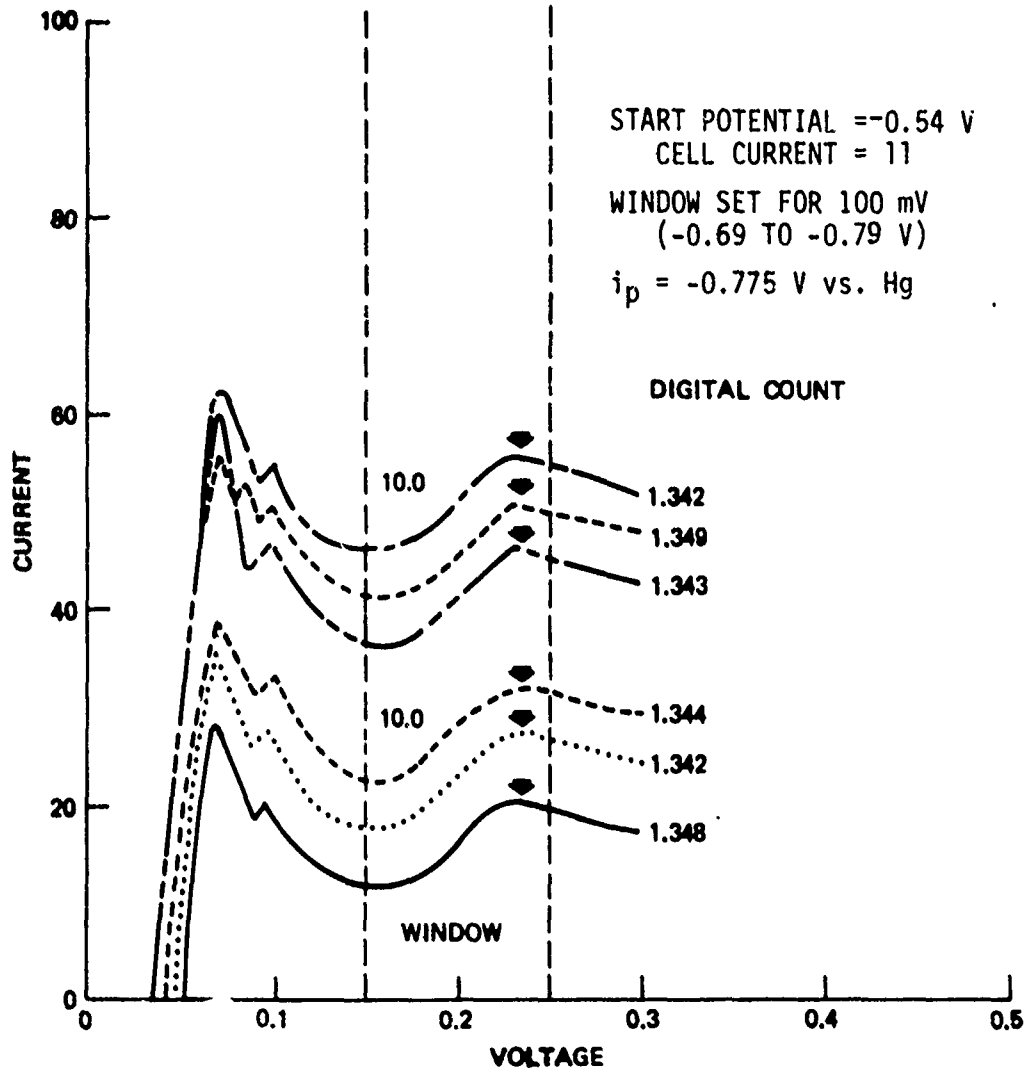
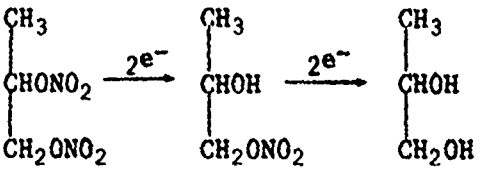


FIGURE 1. Single-Sweep Polarograms Obtained With Solid-State Field Polarograph (0.20 mg/liter PGDN in Effluent Water).



(1,2-PGDN) (1,-PGMN) (PG)

1,2-PGDN gives two waves, i_p = -0.47 V, i_p = -0.85 V (vs. Hg POOL)

1,-PGMN and 2,-PGMN each give one wave, i_p = -0.85 V (vs. Hg POOL)

$$R\text{-}O\text{-}NO_2 \xrightarrow{2e^-} RO^- + NO_2^- \xrightarrow{H^+} R\text{-}OH$$ (see reference 6)

FIGURE 2. Reduction of PGDN at DME (in Effluent Water, pH 6-8).

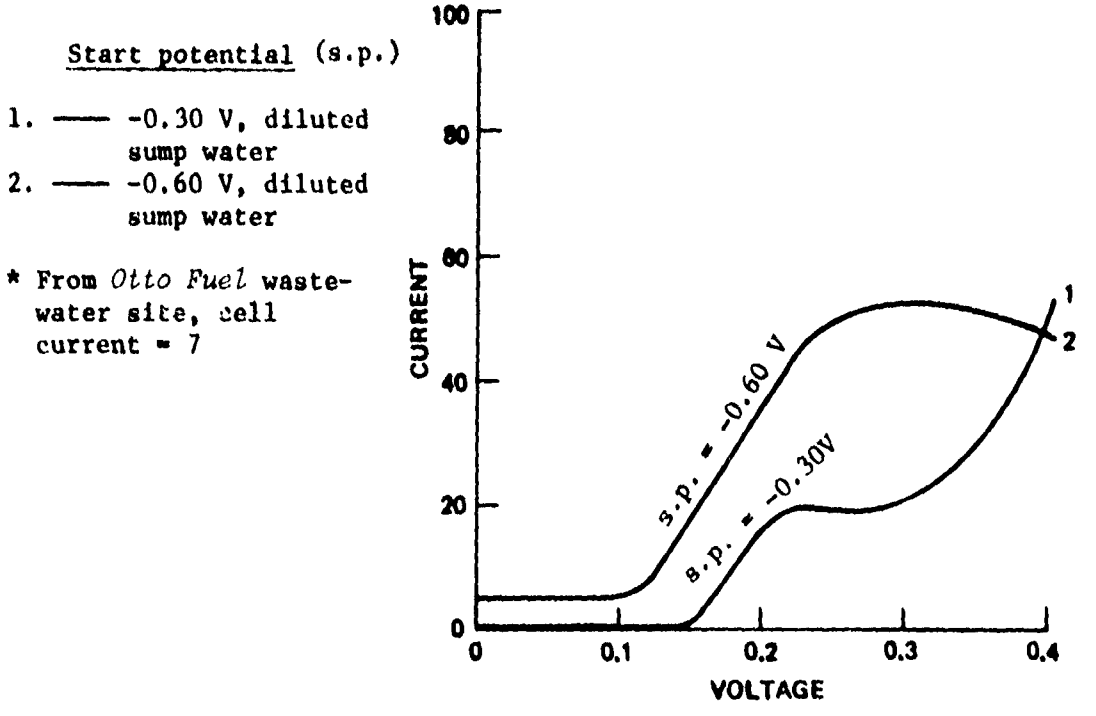


FIGURE 3. Field Polarographic Analysis of Sump Water* (1 ml/100 ml Site Tap Water).

Start potential digital polarograph

1. ——— Original sump water
2. ---- 1.23 mg/liter added PGDN
3. ——— 2.46 mg/liter added PGDN
4. ---- 3.69 mg/liter added PGDN
5. ——— 4.92 mg/liter added PGDN

All curves = -0.60 V

Cell current = 7

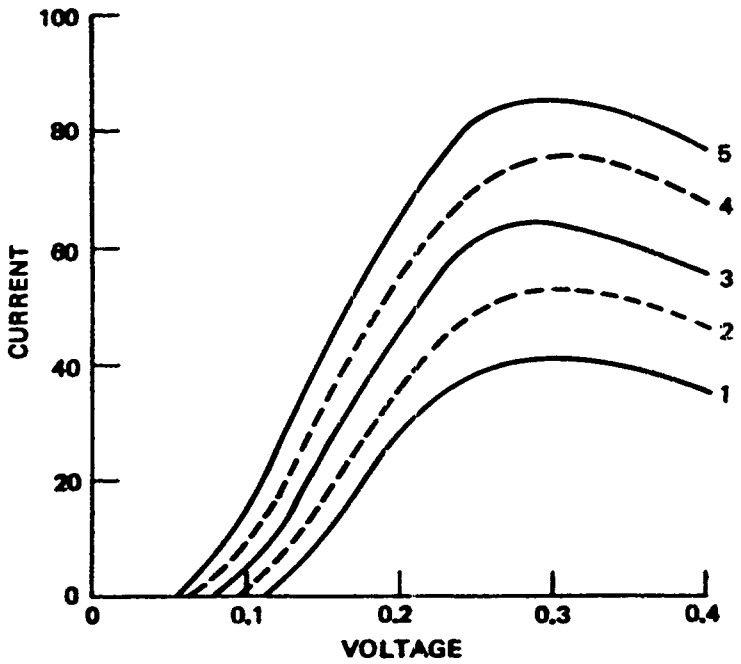


FIGURE 4. Standard Addition of PGDN to Diluted Sump Water (1 ml/100 ml NWC Tap Water, pH 7.80).

SUMMARY

From the operational and analytical data obtained in this series of *field tests* with the NWC digital polarograph and monitoring system, it appears that the instrument package can provide rapid and reliable information at the site. Checks of data for PGDN obtained with both the field polarograph and an NWC research polarograph showed excellent comparison on the same samples of water. The digital polarographic data on the final effluent from the carbon purification system generally agreed well with chromatographic data (vapor-phase) on this water. Some samples of sump water and some column effluent samples showed higher values for PGDN with polarographic analysis than by chromatography. The difference in the analytical data of these samples is thought to be due to the fact that only the polarographic method can measure both PGMN and PGDN. The chromatographic method of analysis used in these studies could not detect PGMN if it was present in the effluent water and thus would give a lower result for PGDN on some samples.

The digital polarograph was carried under the passenger seat of an airplane to Hawaii and Keyport, Washington, respectively, and then by car to the *Otto Fuel* wastewater purification sites. No problems with the performance of the instrument on-site occurred. The instrument was used continuously during an eight-hour day, shut off at night, and turned on the next day. It was used in this manner for a total of 64 hours without any malfunction at the site and after returning to NWC the instrument still operated in a satisfactory manner.

The analytical data obtained at the purification site showed the effluent water from the carbon adsorption purification systems studied to be free of the toxic substances PGDN and/or PGMN within the tolerable limits set for them. The tests successfully illustrated that the NWC polarographic field instrument is very useful for the determination and monitoring on-site of nitrate esters in effluent water produced by carbon cleanup systems.

RECOMMENDATIONS FOR FUTURE WORK

A. The field polarographic monitoring system described in this report operated successfully on-site when used by the author. However, the use of a DME could be troublesome to untrained personnel in the field. The following studies are needed to make the polarographic technique simple enough for untrained personnel to use in the field or put on-line with little or no attention during a cleanup operation of the type described in this report.

1. Prepare a solid-type electrode (glassy carbon, pyrolytic graphite, etc.) whose chemically modified surface responds quantitatively to nitrate esters, nitro compounds, etc. ($C\text{-}ONO_2$, $C\text{-}NO_2$, $N\text{-}NO_2$) under polarographic conditions.

2. Test the chemically modified solid electrode with the digital field polarograph in the laboratory.

3. Test the complete polarographic unit with the new electrode at some typical cleanup sites.

4. Obtain and compare digital polarogrpahic data in the field with other analytical instrumentation data (if available, colorimetric, chromatographic, etc.).

5. If a successful polarographic package results, help install the apparatus and train operators on the use of such instrumentation at field sites.

B. Test the usefulness of the field polarographic monitoring system with other polarographically amenable ordnance-derived pollutants such as trinitrotoluene, dinitrotoluene, cyclotrimethylenetrinitramine, cyclotetramethylenetetranitramine, nitroguanidine, ammonium picrate, etc.

C. Combine high performance liquid chromatography with newly developed electrochemical sensors for increased sensitivity and specificity of pollution monitoring systems. This can provide a most powerful and versatile device.

D. Laboratory and field studies on the hydrolysis of PGDN, both in the sump *Otto Fuel* wastewater and during the operation of a carbon adsorption purification system, should be made. The presence and amount of PGMN in the water should be established by polarography and chromatography. The possibility of other potentially toxic substances remaining in the water from carbon purification systems should be further investigated (organic nitrates, NO_3^-, NO_2^-, $S^=$, SH^-, CN^-, etc.).

E. Samples of the 1- and 2-isomers of PGMN should be prepared, purified, and submitted to toxicity tests. The samples are also needed for analytical studies.

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